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14. ABSTRACT

In the current study the synthesis of hollow gold nanoshells (HAuNS) is demonstrated through the use of a galvanic replacement reaction. HAuNS of select diameter and shell thickness were synthesized and tunability of the extinction coefficient was demonstrated through control of the materials' core–shell ratio.

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1. Introduction and Background

Hollow gold nanoshells (HAuNS) have been synthesized for a number of purposes, including as a near-infrared (NIR) nanoprobe for surface-enhanced Raman spectroscopy,[1] and with tunable sizes for measuring the response to irradiation by femtosecond light pulses in the NIR.[2] The advantage of hollow nanoshells over solid gold (Au) or silver (Ag) nanoparticles, or alloys thereof,[3] is that the absorption maxima of the former can be adjusted from the visible to the NIR by varying the diameter and shell thickness, while the solid Au and Ag surface plasmon resonance (SPR) peaks are at about 520 and 400 nm, respectively. They do red-shift with increasing size, Au more than Ag, but to a much lesser extent than the nanoshells. The paper by Prevo et al.[2] describes a synthesis of HAuNS by starting with Ag sols of varying diameter, and then subjecting them to a galvanic replacement reaction with Au(III). This is essentially a 3-step procedure, which first forms Ag nanoparticles, then grows the diameters at constant particle concentration by adding more Ag(I) and a mild reducing agent. The final step is the addition of tetrachloroauric acid to dissolve the Ag and form the HAuNS.

We report here a variation of the procedure to produce Ag sols of different size in one step, followed by the Au galvanic replacement reaction. In this method, the mass of Ag in the initial formation of the Ag nanoparticles is increased, resulting in a larger diameter, albeit with a likely smaller number concentration.

2. Materials and Methods

2.1 Chemicals

Sodium citrate, silver nitrate (Reagent, 99+ %), sodium borohydride (99.99%), and the gold (III) chloride trihydrate (99.9+ % metal) were all purchased from Sigma Aldrich and used without further purification. All solvents were of high-performance liquid-chromatography grade or higher and used without further purification. Ultrapure milli-Q water was used for all experiments.

2.2 Synthesis of Hollow Gold Nanoshells

The basic synthesis[2] consists of heating 50 mL of a solution 0.2 mM in AgNO3 and 0.5 mM in sodium citrate to 60 °C, followed by rapid addition of 1 mL of a 100-mM sodium borohydride solution into the well-stirred mixture (a 10-fold molar excess of borohydride). The Ag sol forms immediately, resulting in a yellow color and an Ag SPR peak at about 400 nm. The heating and stirring are continued for at least 2 hours (h). To form the HAuNS, 25 mM tetrachloroauric acid is added dropwise to the Ag sol until the 400-nm maximum is gone. Typically, a bit of excess Au(III) was added to ensure complete reaction (an Ag–Au ratio of 2.7 as opposed to the stoichiometric ratio of 3). The resulting HAuNS suspension cooled and was stored in a refrigerator at 4 °C. The authors report this basic procedure yields polydisperse Ag nanoparticles in the 15–25-nm diameter range as measured by dynamic light scattering (DLS). The diameters of the HAuNS formed from this Ag sol were generally in the 20–25-nm range, with an average shell thickness of 7 nm, based on the reported images from transmission electron microscopy (TEM). Larger-diameter HAuNS were made by first growing the Ag sol by adding more silver nitrate and a mild reducing agent to the original Ag sol, resulting in larger-diameter Ag nanoparticles at essentially the same number concentration (10^{10}–10^{11} particles/mL). The HAuNS SPR maximum varied from 565 to 800 nm, red-shifting with increasing diameter at constant shell thickness. The respective colors of the aqueous sols varied from violet through blue to gray with increasing size.

After addition (injection with a syringe) of 1 mL of the 100-mM borohyrdide to the well-stirred solution of 50 mL of silver nitrate (0.2 mM) and sodium citrate (0.5 mM) at 60 °C, the solution turned dark yellow. There was an absorption peak at 390 nm (absorbance [Abs] at 0.32 on the NanoDrop 2000 spectrophotometer) and a slight shoulder at 420 nm. The heating was turned off after 2 h, and the stirring continued overnight. The resulting Ag sol had a slight turbidity, but no visible precipitate. The Ag SPR peak was at 392 nm (Abs 0.25) with a slight shoulder at about 425 nm. The sol was heated to 60 °C and a total of 0.15 mL of 25-mM tetrachloroauric acid added dropwise. This resulted in the complete disappearance of the Ag SPR peak and the appearance of broad peak with an absorption maximum at about 550 nm. The color of this preparation was violet.

The second synthesis was similar to the preceding one, except that a larger concentration of Ag was employed. After addition of the borohydride, the solution turned dark orange with a peak at 382 nm (Abs 0.70), a shoulder at 412 nm, and a slight turbidity. After heating for 1.5 h, the heat was turned off and stirring continued. After 2 h, the color was yellow-orange with a peak at 390 nm (Abs 0.73) and a slight shoulder at 420 nm. After stirring overnight, the sol was orange with a single peak at 390 nm (Abs 0.73), no shoulder, and a slight turbidity. The sol was heated to 60 °C and 25-mM tetrachloroauric acid added dropwise until the 390-nm peak was gone (a total of 0.40 mL). The color was now dark blue with a broad absorption maximum at about 650 nm.

2.3 Material Characterization

Ultraviolet-visible (UV-vis) spectra were obtained on either a Thermo Scientific NanoDrop 2000 or a PerkinElmer Lambda 950 spectrophotometer. The DLS measurements were carried out using a Horiba SZ400 at a scattering angle of 173°. The size and morphology of the HAuNS were determined by TEM and high-resolution TEM using a JEOL JEM-2100F microscope operating at 200 kV and equipped with an Orius SC1000 camera. The compositional analysis was done with energy-dispersive spectroscopy (EDS) using the same microscope. A drop of the HAuNS preparation suspended in water was placed onto a copper grid coated with an amorphous, holey carbon film (200 mesh) and then left drying in air.

3. Results and Discussion

The unfiltered 550-nm absorption-maximum preparation was examined by DLS, yielding an average diameter of 119 nm. After passing the sol through a 0.22-micron syringe filter, the diameter was 46 nm. However, TEM examination of the sol deposited on a grid yielded an average diameter of 12.8 nm with a standard deviation of 4.4 nm. DLS provides a so-called z-average diameter, which heavily weights larger particles. The TEM measurements (Fig. 1) show that the interior is indeed hollow. The HAuNS are polydisperse as shown by a range histogram derived from the TEM pictures (Fig. 2). However, no particles larger than 19 nm in diameter were observed. This indicates that some larger, extraneous particles were still present. The average shell thickness was 4.4 nm.

The unfiltered 650-nm absorption-maximum preparation yielded an average DLS diameter of 129 nm; then, 47 nm after passing through the 0.22-micron filter. The TEM results gave an average diameter of 21.7 nm, with a standard deviation of 7.2 nm and a polydispersity greater than that of the 550-nm sol (Fig. 2). The average shell thickness was 4.7 nm, essentially the same as that of the 550-nm preparation. The difference in the SPR absorption maxima of the 2 preparations can therefore be ascribed to the difference in particles' diameters.

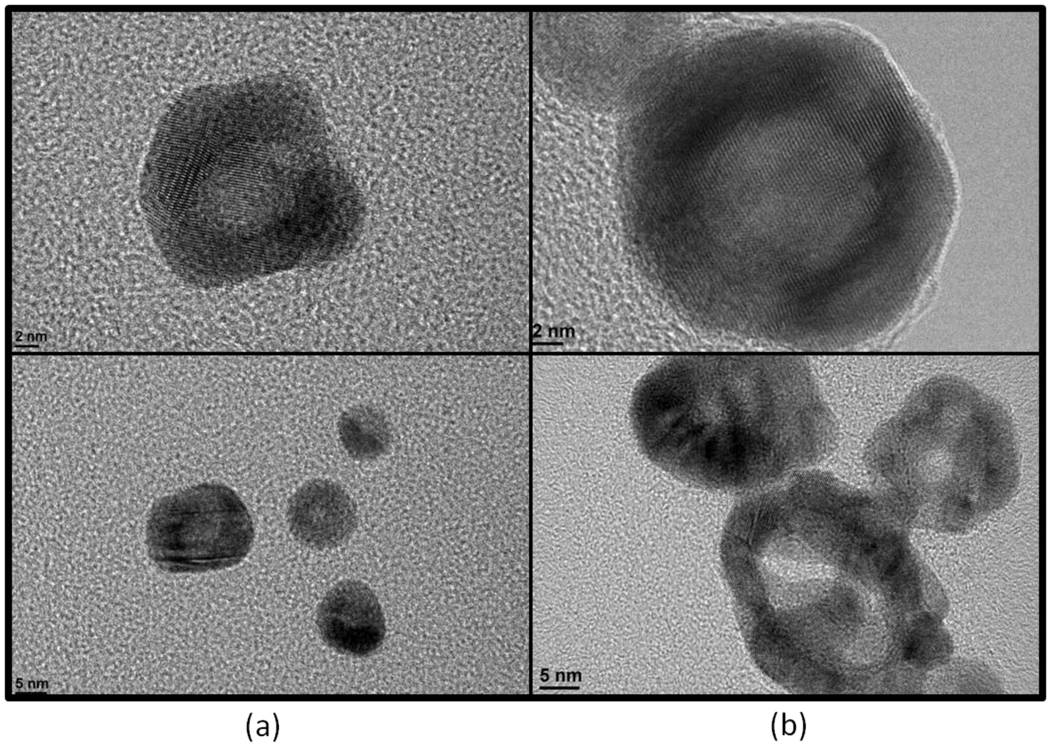

Fig. 1 **TEM images of the a) 550-nm and b) 650-nm extinction peak HAuNS**

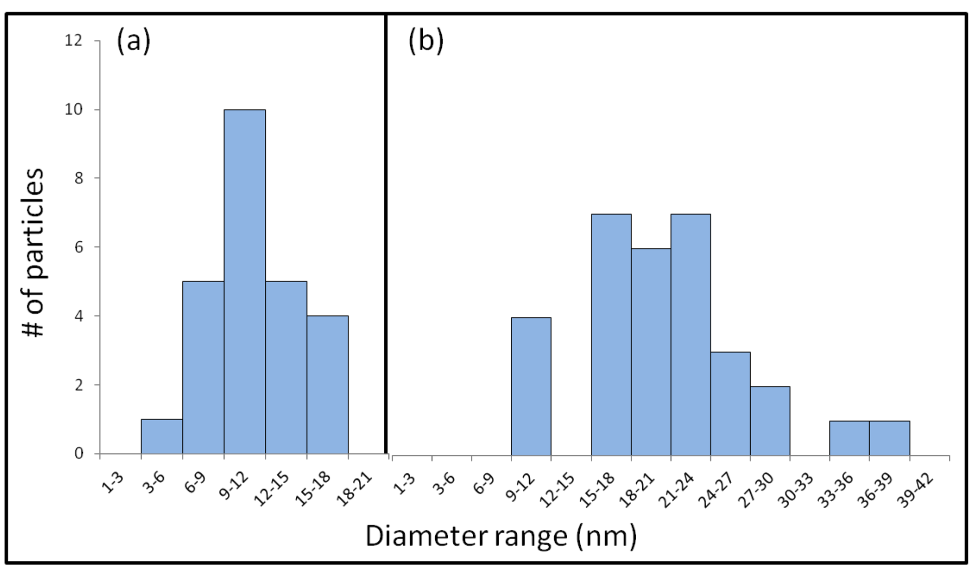

Fig. 2 **Histogram of TEM diameters for the a) 500-nm and b) 650-nm HAuNS**

There is residual Ag present in both sols as evidenced by EDS (e.g., Au–Ag ratio of 75:25, but some variation depending on location). Residual Ag that could not be removed by dialysis was also found by Prevo et al.[2] Based on the calculated number concentration of nanoshells, the extinction coefficients are on the order of

$10^9 M^{-1} cm^{-1}$. The lower number concentration of the larger HAuNS is approximately compensated by the higher extinction efficiency of these shells.

After storage for 70 days in a refrigerator at 4 °C, the HAuNS sols were re-examined, with the corresponding UV-vis spectra shown in Fig. 3. The larger sol has an absorption maximum at 654 nm, essentially unchanged from the freshly prepared one. TEM also shows that the particle-size range is comparable. However, the absorption maximum of the smaller sol has shifted from 550 nm to 507 nm, in addition to developing a broader absorption full width at half maximum—suggesting an increase in sample polydispersity. TEM shows a somewhat larger particle-size range, but this should cause a red shift as opposed to the observed blue shift. It is possible that alloying of the residual Ag with the Au occurred. Such alloys exhibit a blue shift compared with solid Au nanoparticles.[3] However, this would require that alloying of the 550-nm sol, but not the 650 nm sol, took place while in cold storage. The surface composition, including adsorbed species, can shift the absorption maximum, and the ratio of citrate and borohydride to Ag was greater in the small sol. It is clear that the explanation of this effect requires further study.

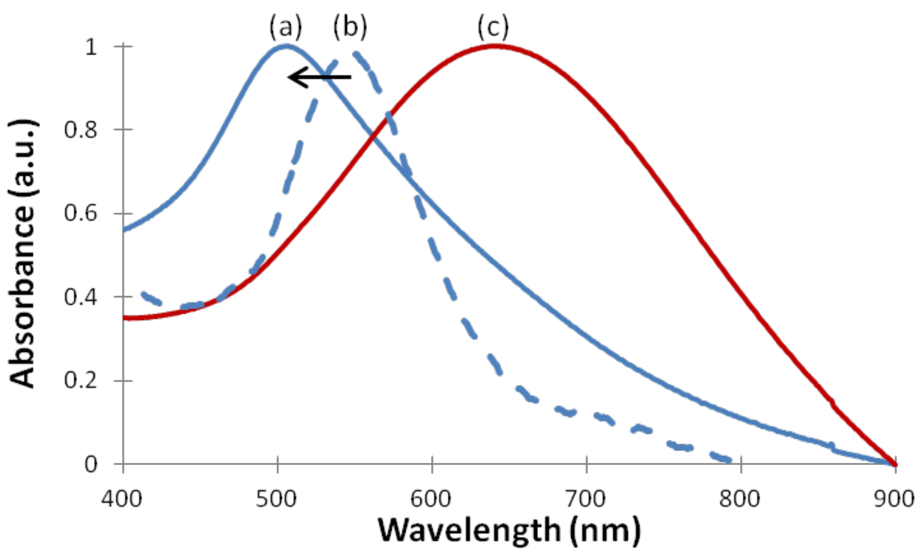

Fig. 3 UV-vis spectra of the a) blue-shifted HAuNS after aging for 70 days, b) original 550-nm emission sample, and c) 650-nm HAuNS aged for 70 days at 4 °C following synthesis

Finally, it should be noted that during the synthesis of the starting Ag sol a longer wavelength shoulder on the main SPR peak initially formed; it either vanished or decreased significantly after stirring overnight. If this were due to a population of larger Ag nanoparticles, Ostwald ripening would be expected to cause an increase, not a decrease, in size. It is possible that some loose aggregation was initially present, which was broken by continued stirring. Whatever the explanation, its effect on the synthesis is unclear. It may contribute to a greater polydispersity, another aspect of this synthesis worthy of further study.

4. Summary and Conclusions

HAuNS of increasing size, and corresponding longer absorption wavelengths, can be produced from starting Ag sols by galvanic replacement with Au. Larger Ag nanoparticles, resulting in larger HAuNS, can be synthesized in one step by increasing the initial Ag concentration. However, the resulting polydispersity of the nanoshells increases. This may or may not be important, depending upon the intended application. It may be possible to mitigate this effect by employing a more rapid mixing regime, varying the concentration of stabilizer and/or reducing agent, or both.

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List of Symbols, Abbreviations, and Acronyms

Abs	absorbance
Ag	silver
ARL	US Army Research Laboratory
Au	gold
DLS	dynamic light scattering
EDS	energy-dispersive spectroscopy
h	hour
HAuNS	hollow gold nanoshell
NIR	near-infrared
SPR	surface plasmon resonance
TEM	transmission electron microscopy
UV-vis	ultraviolet-visible

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